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HIGH ENERGY MATERIALS. NEW PREPARATION APPROACHES TO NITRO AND --ETC(U)
JUN 81 J H BOYER, T P PILLAI N00014-79-C-0353

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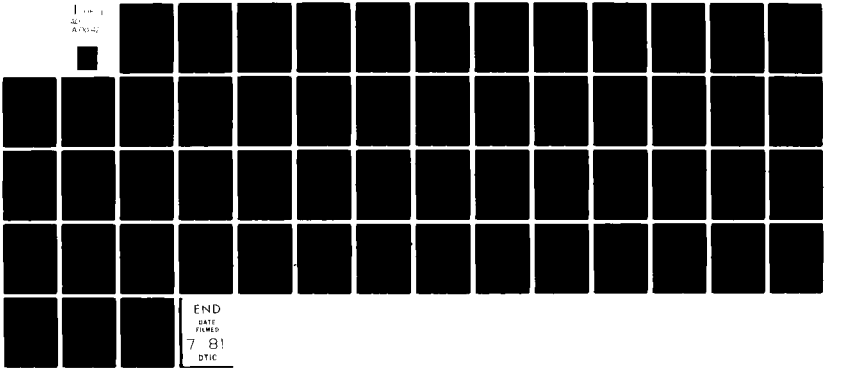

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Hydrazine and hydroxylamine efficiently transformed dicyanofuroxan into pyridazino- and oxazinofuroxans. Product identification has clarified the reaction between iodoacetonitrile and silver nitrate. A series of azepine oxides was obtained from peroxidation of aldimine derivatives of diamino-maleonitrile. Nitrobenzofuroxans were peroxidized into polynitrobenzene compounds; benzodifuroxan was peroxidized into 1,2,3,4-tetranitrobenzene. Investigations on 2-nitroso-3-nitrosuccinonitrile, 2,3-dinitrosuccinonitrile and related compounds are underway.

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HIGH ENERGY MATERIALS. NEW PREPARATION APPROACHES TO NITRO AND NITROSO DERIVATIVES.

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Part I

Dicyanofuroxan and Hydrazine or Hydroxylamine

By Joseph H. Boyer and T. Perumal Pillai

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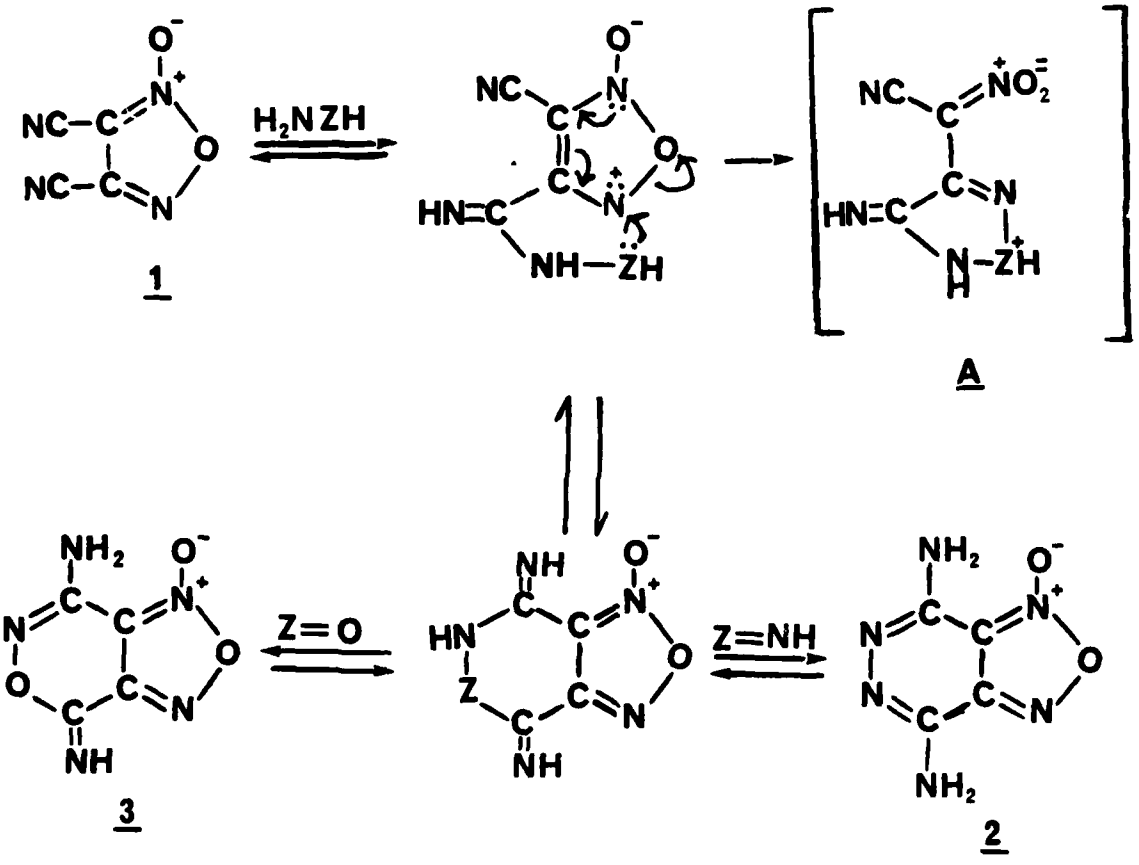
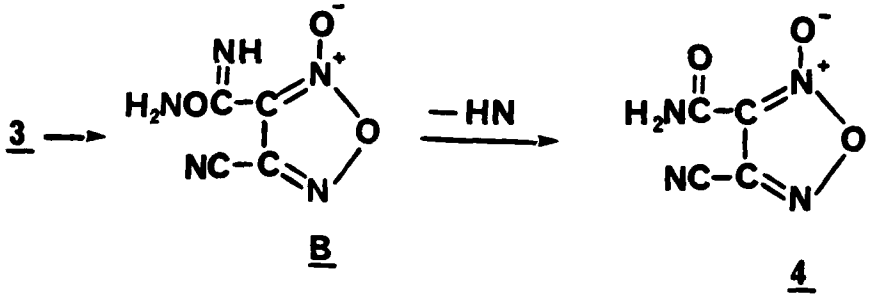
Summary. Dicyanofuroxan combined with hydrazine to produce 1,4-diamino[4,5-c]pyridazinofuroxan 2 and with hydroxylamine to produce the imine 3 of 1-oxo-4-amino [4,5-c]oxazinofuroxan; mild thermolysis of the latter adduct gave 3-cyano-4-carbamoyl furoxan 4.

Dicyanofuroxan 1, a synthon of considerable potential for high energy compounds with low hydrogen content, has received only minor attention, a reflection of its explosive nature.[1] An extremely vigorous reaction with hydrazine[1] or hydroxylamine can be controlled by adequate cooling. When run in dimethylformamide near 0°C the reaction with hydrazine gives 1,4-diamino [4,5-c]pyridazinofuroxan 2 and with hydroxylamine the imine 3 of 1-oxo-4-amino[4,5-c]oxazinofuroxan. Competitive attack on the furoxan ring was unproductive,

but nevertheless assumed, since benzofuroxans are (1) reduced into dioximes by hydrazines[2] or hydroxylamine,[3] and (2) transformed into o-nitrophenyl hydrazines by secondary amines.[4] When uncontrolled this reaction may lead to internal nitronates, e.g. A, an often unstable species,[5] and their explosion.



Moderate heat transformed the oxazinofuroxan 3 into 4-cyano-5-carbamoylfuroxan 4, presumably by the loss of imidogen from an O-imidoylhydroxylamine B, a tautomer of 3.[6]



To dicyanofuroxan (1.0 g, 8.0 mmole) in dimethylformamide(DMF) 30 ml) at 0°C, hydrazine hydrate (85% 0.8 g, 16 mmole) in DMF (5 ml) was added dropwise for over 0.5 hour with stirring which was continued for 2 hours. Crushed ice was added and the aqueous solution was extracted with ether. The residue after removal of the ether recrystallized from a mixture of ethyl acetate and hexane as the pyridazinofuroxan 2, a yellow solid, 67% mp 118-119°C (dec); satisfactory analysis for C, H and N; ir(KBr): 3460 (m), 3370 (m) and 1600 cm^{-1}(s); nmr($(CD_3)_2CO$): δ 6.4 (broad singlet, exchanged with (D_2O); m/e (70 eV)(%): 168(100) M , 152(5), (151(5), 139(70), 138(15) and 108(90). The substitution of a

molar equivalent of hydroxylamine for hydrazine, and methylene chloride for ether in extraction afforded the oxazinofuroxan 3 as a colorless solid, 78%, mp 143-144°C (dec); satisfactory analysis for C, H and N; ir (KBr): 3470 (m), 3360 (m) and 1610 cm^{-1}(s); nmr ($(CD_3)_2CO$): δ 5.9 (exchangeable with D_2O); m/e (70 eV)(%): 169(5) M^+, 168(100), (153(5), 138(10), 109(90). Heating in a mixture of ethyl acetate and hexane brought about the change 3 → 4. The amide 4 was obtained as a colorless solid, mp 178-179°C (dec);[7] ir (KBr): 3390 (m), 3300 (w), 3220 (m), 2250 (s), 1700 (s), 1620 (s), 1600 (s), 1485 (m), 1375 (m), 1065 (m), 1030 (m) and 840 cm^{-1} (m): nmr ($(CD_3)_2(CO)$: δ 7.85 (broad, exchangeable with D_2O); m/e (70 eV)(%): 154(100) M^+, 139(5), 124(50), 112(50), 111(90), 109(30), 95(5) and 92(5); satisfactory analysis for C, H and N.

Acknowledgment. Financial support was received from the Office of Naval Research.

1. R. H. Homewood, V. J. Krukonis and R. C. Loszewski, U. S. 3,832,249; Chem. Abstr. 1975, 82, 113795z. D. D. Denson and F. M. VanMeter, U.S. 3,740,947; Chem. Abstr., 1973, 79, 94195y.

2. M. M. El-Abadelah, Z. H. Khan and A. A. Anani, Synthesis, 1980, 146.

3. J. H. Boyer and W. Schoen, J. Amer. Chem. Soc., 1956, 78, 423.

4. D. W. S. Latham, O. Meth-Cohn and H. Suschitzky, J. Chem Soc. Perkin I, 1976, 2216.

5. A. T. Nielsen, "Nitronic Acids and Esters," in "The Chemistry of the Nitro and Nitroso Groups," ed. H. Feuer (ser. ed. S. Patai), Interscience, New York, 1969, p 351 ff.

6. C. Walling and A. N. Naglieri, J. Amer. Chem. Soc., 1960, 82, 1820 reported the thermolysis of an O-acylhydroxamate: $C_6H_5CONHOCOC_6H_5 \rightarrow C_6H_5CO_2H + C_6H_5CON(\rightarrow C_6H_5NCO)$.

7. C. Grundmann, G. W. Nickel and R. Bansal, Liebig's Ann. Chem., 1975, 1029 reported mp 182-184°C (dec).

Part II

O-Cyanomethyloxime of Nitroglyoxylonitrile

By T. Perumal Pillai and Joseph H. Boyer*

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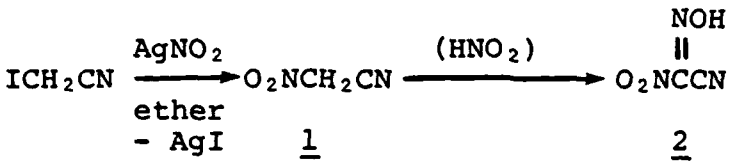
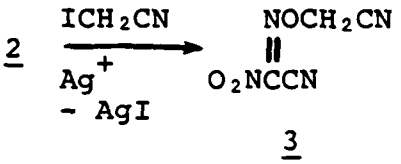
Summary: The O-cyanomethyloxime 3 of nitroglyoxylonitrile was obtained from iodoacetonitrile and silver nitrate in ether and transformed in warm water into the O-cyanomethyl ether 4 of the oxime derivative of cyanomethyl cyanoformate.

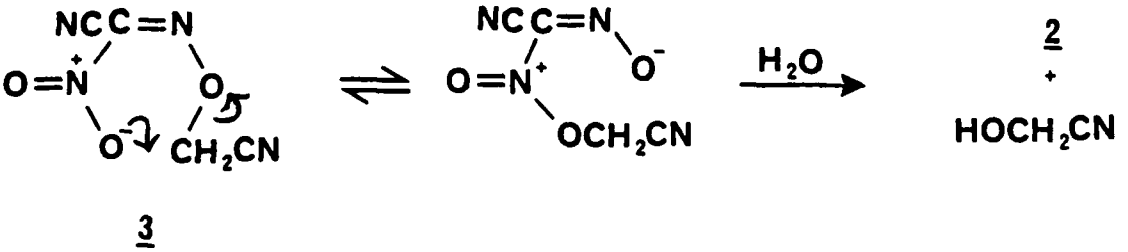
The formation of the O-cyanomethyl ether 3 (a nitrolate ester) of the oxime of nitroglyoxylonitrile from iodoacetonitrile and silver nitrite is, to our knowledge, the only example of a preparation of a nitrolate ester which does not require starting with an α-nitronitronate ester or anhydride.[1-3]

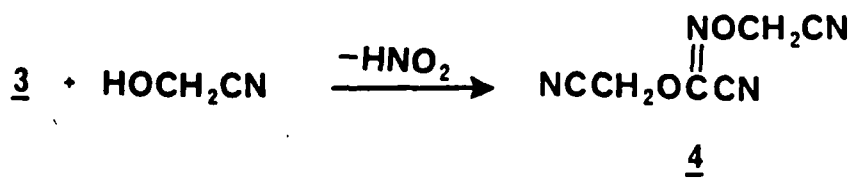
Nitrosation of unisolated nitroacetonitrile 1 is considered to be a key step in an account of the formation of the nitrolate 3.[4] Alkylation of the nitrolic acid 2 by iodoacetonitrile occurred preferentially at the oxime oxygen atom, a consequence of retarded alkylation at the oxime nitrogen atom by electron withdrawal into the cyano and nitro groups.[5] The liquid nitrolate ester 3 (44%) was the only product isolated.[6]





A facile reation with water is a property of a nitrolic acid[7] apparently shared with an ester derivative. The transformation of the ester 3 in warm water into the O-cyanomethyl ether 4 (48%), mp 70-71°C,.[1] of the oxime derivative of cyanomethyl cyanoformate is attributable to a nucleophilic displacement of the nitro group in the ester 3 by the cyanohydrin of formaldehyde presumably generated by an intermediate fragmentation and hydroloysis[8] of the nitrolate 3.





$$\underline{2} \xrightarrow{H_2O,\Delta} HCN + CO_2 + (NOH)_2 \quad (N_2O + H_2O)$$

Acknowledgement: Financial support was received from the Office of Naval Research.

1. R. Scholl (Chem. Ber., 1896, 29, 2415) reported the reaction between iodoacetonitrile and silver nitrite but incorrectly identified compound 3 as dicyanomethazonic acid. He also obtained compound 4, $C_6H_4N_4O_2$, but did not assign a structure. With very minor modifications his directions have been repeated. Satisfactory analyses for C, H and N were reobtained for compounds 3 and 4.

2. A. T. Nielsen, "Nitronic Acids and Esters", in "The Chemistry of the Nitro and Nitroso Groups", ed. H. Feuer in "The Chemistry of Functional Groups", ser. ed., S. Patai, Interscience, New York, 1969, pp 423, 445, 458, 467 and 468. Transformations of nitronates ($RC(NO_2)=NO_2R$) into nitrolates ($RC(NO_2)=NOR$) are discussed.

3. I. E. Chlenov, N. S. Morozova, V. A. Tartakovskii, and S. S. Novikov (Izv. Akad. Nauk SSSR, Ser. Khim., 1969, 2226; Eng. trans., 1969, 2113) have reported

examples of 3-nitroisoxazolines, $O_2NC{=}N{-}O$.

4. Nitroglyoxylonitrile oxime 2 (a nitrolic acid) was obtained from nitroacetonitrile and sodium nitrite (W. Steinkopf, Chem. Ber., 1909, 42, 617).

5. P.A.S. Smith and J.E. Robertson, J. Amer. Chem. Soc., 1962, 84, 1197.

6. Compound 3. Ir(CH_2Cl_2): 3005(w,CH_2), 2220(w,C≡N), 1605(s,C=N),1570(s,NO_2) and 1340 cm (m,NO_2); nmr ($CDCl_3$): δ 5.2(s, not exchangeable with D_2O); ^{13}Cnmr ($CDCl_3$):δ 125.49(-N=C), 113.01(NC-CH_2), 103.24(=C-CN) and 63.89 ppm (OCH_2), split into 3s in the non-decoupled spectrum; m/e(70 ev)(%): 154(50) M^+, 151 (100), 138(50), 137(50), 127(45), 126(35) and 109 (45).

7. P.A.S. Smith, "Open-chain Nitrogen Compounds", W. A. Benjamin, Inc., New York, 1966, Vol II, p 431.

8. Compound 4. Ir(CH_2Cl_2): 2250(w,C≡N) and 1615 cm^{-1} (m,C=N); nmr($CD_3)_2CO$): δ 5.13(s, CH_2) and 5.26 (s,CH_2), neither exchangeable with D_2O); δ ^{13}Cnmr ($CDCl_3$ and $(CD_3)_2SO$): δ 138.28(N=C), 115.10(C=N), 113.35(CN), 105.53(=C-CN, 60.93(OCH_2) and 54.42 (OCH_2); m/e (70ev)(%): 164(15) M^+, 138(10, 134(20), 109(5), 107(10), 104(20), 94(90), 84(20) 80(80) and 79(100).

Part III

BICYCLIC PEROXIDES FROM A 1,4-DIAZEPINE

V. T. Ramakrishnan† and Joseph H. Boyer*

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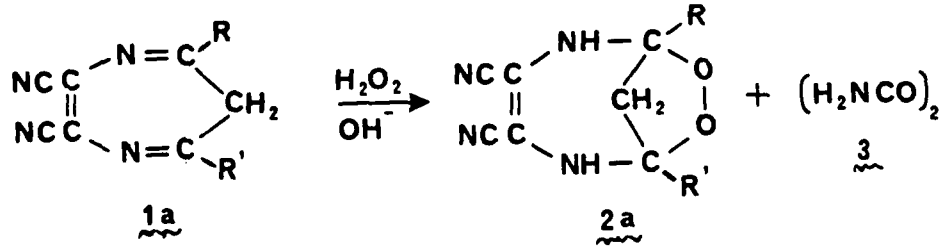
Abstract - An adduct, 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]non-3-ene, was obtained from 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine and hydrogen peroxide in the presence of alkali or a tertiary amine. It was dehydrogenated by iodobenzene diacetate into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]nona-2,4-diene; further oxidation by m-chloroperbenzoic acid gave 4,5-dicyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo[6.2.1.$0^{2,4}0^{5,7}$]undecane.

Hydrogen peroxide in the presence of sodium hydroxide or pyridine in methanol, or hydrogen peroxide in acetonitrile efficiently transformed 2,3-dicyano-5,7-dimethyl-6H-1,4-diazepine 1a[1] into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo [4.2.1]-non-3-ene 2a,[2] the first example of a bicyclic peroxide from a diazepine. Oxamide was a minor by product. In the absence of an alkali or an amine the reaction in methanol gave traces of the adduct 2a and larger amounts of oxamide and 2,4-pentanedione. Peracids, e.g., m-chloroperbenzoic(MCPBA) or trifluoroperacetic acids, either failed to react with the diazepine 1a under mild conditions or gave intractable mixtures under more severe conditions. The detection of an isocyanide odor during peroxidation of diazepine 1a is being investigated.



1a 2a 3

a, R = R' = CH_3; b, R = R' = C_6H_5; c, R = C_6H_5, R' = CH_3

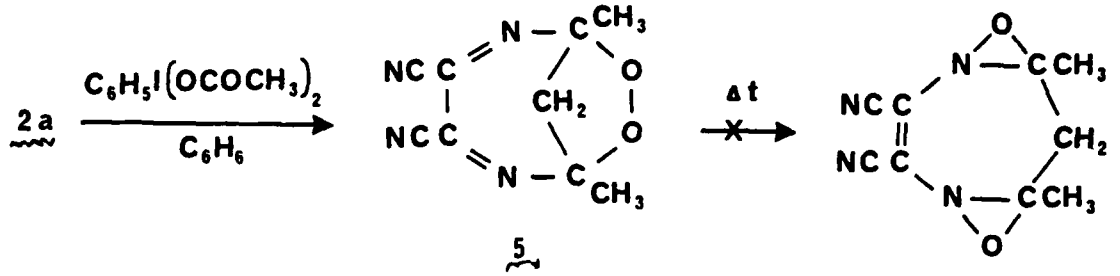
Anticipated reactions between a hydroperoxide and a diazepine apparently did not occur since neither an oxaziridine,[3-5] a nitrone,[3] an amide (other than oxamide),[6] simple ring cleavage,[7] nor ring contraction[8] was detected. The formation of oxamide 3, was attributed to the hydration of cyanogen,[9] a degradation intermediate, by aqueous peroxide. Attempts to obtain peroxides 2b,c from diazepines 1b,c, and to obtain 2,3-dicyano-5,6,6,7-tetramethyl-6H-1,4-diazepine from 3,3-dimethylpentane-2,4-dione and diaminomaleonitrile by an adaptation of the preparation of the azepine 1a[1] were unsuccessful.

The peroxide structure 2a was directly supported by ir spectroscopic detection of NH, C≡N and C=C functions, by ^{1}H and ^{13}C nmr detection of methyl and methylene protons and carbon atoms in CH_3, CH_2, CO and CN functions; by molecular weight determination and by elemental analysis. On standing in methanol (25°C, 90 hours), or on heating neat above 125°C (dec) the peroxide 2a fragmented into 2,4-pentanedione and presumably diiminosuccinonitrile 4, a precursor to cyanogen and oxamide 3. The latter was also obtained (47%) from the cyclic peroxide 2a and hydrogen peroxide in methanol (25°C, two days). Triphenylphosphine converted the peroxide 2a into the diazepine 1a.

$$(CH_3CO)_2CH_2 + \underset{4}{\left[(HN{=}C(CN))_2\right]} \xleftarrow{\Delta t} 2a \xrightarrow{(C_6H_5)_3P} 1a + (C_6H_5)_3PO$$

$$2a \xrightarrow[25^{\circ}C,\ 48\ h]{CH_3OH,\ H_2O_2} \left[4 \xrightarrow{-2\ HCN} (CN)_2\right] \xrightarrow[H_2O_2]{H_2O} 3$$

Iodobenzene diacetate in benzene quantitatively dehydrogenated the peroxide 2a into 3,4-dicyano-1,6-dimethyl-2,5-diaza-7,8-dioxabicyclo[4.2.1]nona-2,4-diene 5 (see Experimental Section for confirmation data). Without a trace of isomerization into a bisoxaziridine 6, thermolysis again gave 2,4-pentanedione but the remaining mixture was intractable. During chromatographic separation from silica gel hydration of the dicyanide 5 gave the diamide 7, whereas an azomethine adduct 8 was obtained from methanol containing sulfuric acid. The diazepine 1a was produced in small amounts from the peroxide 5 and triphenylphosphine.



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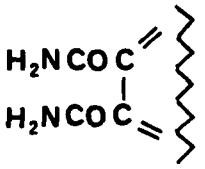

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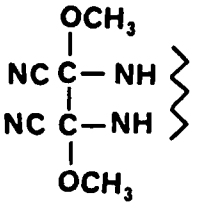

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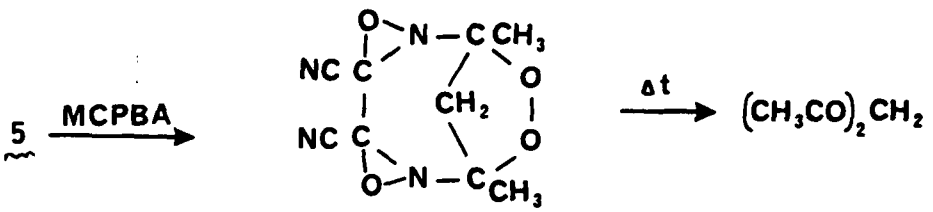
m-Chloroperbenzoic acid(MCPBA) converted the bisimine 5 into 4,5-dicyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo[6.2.1.$0^{2,4}0^{5,7}$] undecane 9 in moderate yield. The assigned structure was supported by spectroscopic and other analytical data (see *Experimental Section*). *Thermolysis* gave 2,4-pentanedione and intractable material. Neither an epoxide of the olefin 6[10] nor dicyanofuroxan 10, an expected fragmentation product, was detected.



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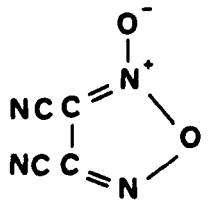

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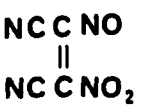

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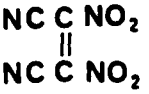

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Intractable mixtures were obtained from the bisoxaziridine 9 by thermolysis and by further treatment with peroxides. The formation of either a nitrosonitro- 11 or a dinitromaleonitrile 12 was not established. Triphenylphosphine deoxy-

genated the cyclic peroxide 9 into the diazepine 1 in small amounts.

Acknowledgements: Financial support from O.N.R. FD mass spectra from the School of Chemical Sciences, University of Illinois, Urbana, Illinois.

Experimental

Instruments included Perkin Elmer 237B and 521 grating i.r.; Varian A-60 n.m.r.; and Varian MAT 731 FD mass spectrometer. Selected m/e(70 eV) values and all FD values are reported. Each yield was based on starting material consumed. Elemental analyses were provided by Micro-Tech Laboratories, Skokie, Illinois.

Preparation of the diazepine 1a: A condensation between diaminomaleonitrile and 2,4-pentanedione gave the diazepine, mp 202-204°C (dec); ^{1} ^{13}Cnmr ($(CD_3)_2SO$): δ 26.2 (CH_3), 49.4(CH_2), 115.3(C≡N), 122.9(C=C) and 158.3(C=N).

Preparation of the cyclic peroxide 2a: To an ice-cooled stirred suspension of the diazepine 1a (8.0g,46.5 mmoles) in methanol(100 ml) was added a few drops of 1 N sodium hydroxide solution followed by dropwise addition of 90 percent hydrogen peroxide (2.8 ml,100 mmoles). The mixture was stirred until the disappearance (about 3 h) of the diazepine 1a (tlc) left a clear yellow solution. The reaction mixture was concentrated at a temperature below 45°C until a crystalline solid 2a appeared. Dilution with ice-water brought further separation of the peroxide 2a as a light yellow solid which was filtered and dried at room temperature, 7.2g(75%), mp 125-6°C(dec) (ethyl acetate and hexane); ir(KBr):3333(NH), 2222(CN), 1634(C=C) cm^{-1}; ^{1}H-nmr (acetone-d_6): δ 1.68 (s), 2.5-3.2 (m) and 6.57 (br); (D_2O): δ 1.68 (s,6H), and 2.53-3.05 (2H, AB quartet, J = 12 Hz); ^{13}C-nmr (acetone-d_6): δ 23.90 (CH_3), 57.57 (CH_2), 94.40 (C-O), 105.49 (C=C) and 116.95 (CN); m/e (70 eV) (%):206(6) (M^+), 100(100), 85(100); m/e(FD): 206(100)M^+; found: C, 52.08; H, 4.85; N, 27.03 %; $C_9H_{10}N_4O_2$ requires C, 52.42; H, 4.85; N, 27.18 %.

Efficient cooling during slow addition of the hydrogen peroxide to the diazepine 1a controlled an otherwise violent reaction and prevented the formation of oxamide. Both higher temperatures and complete evaporation of the solvent in the rotary evaporator led to product decomposition. The peroxide 2a was stable on refrigeration but exposure to the atmosphere or storage at room temperature brought about blackening and apparent polymerization. The peroxide was also produced (80%) in acetonitrile at room temperature for 17 hours. In methanol the

formation of oxamide predominated on prolonged reaction time, with or without added pyridine. After the peroxide 2a in methanol was stirred at room temperature for 90 hours, 2,4-pentanedione but not the peroxide 2a was detected (tlc).

Treatment of the peroxide 2a (100 mg, 0.5 mmol) with hydrogen peroxide (90%,0.8 ml) in methanol at room temperature for 20 hours gave oxamide (47%), 2,4-pentanedione (tlc) and the odor of an isocyanide.

To a solution of triphenylphosphine (700 mg, 2.7 mmoles) in benzene (25 ml) the peroxide 2a (500 mg, 2.5mmoles) was added and the mixture stirred for 17 hours. The separated colorless solid was filtered and washed with benzene and was identified (tlc) as the diazepine 1a (300 mg, 72 %) mp and mixture mp 201-3°C.

Preparation of the bisimine 5: To a stirred suspension of iodobenzenediacetate (4.0 g, 12 mmoles) in benzene (100 ml) the cyclic peroxide 2a (2.0 g, 10 mmoles) was added in portions. The reaction mixture was stirred for 64 hours at room temperature and filtered to remove unidentified solid material (90 mg). The filtrate on concentration and addition of hexane gave the bisimine 5 as a light yellow solid, 1.7 g(85 %), mp 161-3°C (ethyl acetate and hexane), dec around 170°C; ir ($CHCl_3$): 2230 (CN), 1628, 1588 cm^{-1}; ^{1}H-nmr($CDCl_3$-acetone-d_6): δ 1.86(s, 6H, $2CH_3$) and 3.20(s, 2H, CH_2); ^{13}C-nmr($CDCl_3$-DMSO-d_6): 23.24 (CH_3), 50.93 (CH_2), 96.58 (C-O), 114.75 (CN), and 136.62 ppm (C=N); m/e (70 eV) (%); 172(52), 163(7), 131(100), 100(15), 91(85); m/e (FD): 204(100)M^+, 172(90), 163(10) and 100(10); found: C, 52.67; H, 4.05; N, 26.86; O, 16.69; $C_9H_8N_4O_2$ requires: C, 52.94; H, 3.95; N, 27.44; O, 15.67 %.

Preparation of the bisepoxide 9: To a stirred suspension of m-chloroperbenzoic acid (2.2 g, 12.8 mmoles) in acetone (100 ml) the bisimine 5 (980 mg, 4.8 mmoles) was added in portions at room temperature. The reaction mixture was stirred for 3 hours and concentrated. The residue was dissolved in ethyl acetate, washed with aqueous sodium bicarbonate solution and dried ($MgSO_4$). Removal of solvent furnished a solid (1.0 g) which showed three tlc spots. Chromatography over a silica gel column (25 x 2 cm) gave di-(m-chlorobenzoyl)peroxide, mp 118-120°C(dec)(lit.[11] mp 122-3°C, 80 mg, also obtained from a sample of MCPBA on elution with a mixture of chloroform and hexane (1:9). Elution with a 3:7 mixture of chloroform and hexane gave the bisoxaziridine 9 (200 mg, 17.7 %) as a colorless solid, mp 117-8°C(chloroform-hexane); 140-145°C (dec); ir (CH_2Cl_2): 2245 cm^{-1}

(CN); ^{1}H-nmr ($CDCl_3$); δ 1,72 (s,3H), 1.83 (s,3H) and 2.50-3.15 (AB quartet, 2H, J = 15 Hz); ^{13}C-nmr ($CDCl_3$): δ 20.11 (CH_3), 25.07 (CH_3), 49.31 (CH_2); 74.97 (C-CN) 97.17 (CH_3CO) and 101.88 (CN); m/e (70 eV) (%): 204(1), 100(100); m/e (FD): 237 (100)(MH^+), 186(23), 100(85); found: C, 45.79; H, 3.40; N, 23.85; $C_9H_8N_4O_4$ requires C, 45.77; H, 3.41; N, 23.72%.

Elution with chloroform gave a semisolid (360 mg) which on trituration with a mixture of ethyl acetate and hexane gave a colorless solid, mp 147-9°C (dec) (chloroform-hexane); found: C, 45.17 and 45.22; H, 4.23 and 4.26; N, 19.88 and 19.65; $C_8H_9N_3O_4$ requires: C, 45.50; H, 4.30; N, 19.90 %. It has tentatively been identified as 4-cyano-1,8-dimethyl-2,7-diaza-3,6,9,10-tetraoxatetracyclo [6.2.1 $O^{2,4}$ $O^{5,7}$]undecane, cf. 9 with one cyano group replaced by hydrogen, and will be further investigated.

Preparation of the methanol adduct 8: The bisimine peroxide 5 (100 mg) was dissolved in methanol (5 ml) and a drop of dilute sulfuric acid added. A colorless solid started to separate gradually. After stirring for 17 hours, the reaction mixture was concentrated, diluted with water and filtered to isolate the bis methanol adduct 8 as a colorless solid; 70 mg (52 %); mp 188-190°C (dec) (methanol); ir (KBr): 3330, 2230, 1520, 1495 cm^{-1}; ^{1}H-nmr (DMSO-d_6); δ 3.36 and 3.41 (2 s,6H), 5.6 and 5.7 (2 broad s, 2H, exchanged with D_2O), 2.2-3.0 (AB quartet partly hidden in DMSO peaks, J = 12.5 Hz) and 1.4 (s,6H); m/e (70 eV) (%): 236(18), 235(100), 100(80), 85(100); m/e(FD): 268(100)M^+, 236(10), 235(34) and 98(12); found: C, 49.06; H, 5.95; N, 20.77; $C_{11}H_{16}N_4O_4$ requires C, 49.25; H, 6.01; N, 20.88 %.

A solution of the bisimine 5 (400 mg, 2 mmoles) in benzene (50 ml) was treated with triphenylphosphine (1.05 g, 4 mmoles) added in portions. The reaction mixture turned red-brown. A solid which separated over several hours with stirring was triturated with benzene and ethanol to give the diazepine (tlc) 1a, mp and mixture mp 200-202°C.

+On leave from University of Madras, P.G. Centre, Coimbatore, 641041, India.

References and footnotes.

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7. N. Murugesan and M. Shamma, Tetrahedron Lett., 1979, 4521 reported an opening of a pyridinium ring initiated by an attack by m-chloroperbenzoic acid at an azomethine carbon atom.

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Part IV

OXIDATION OF NITROBENZOFUROXANS

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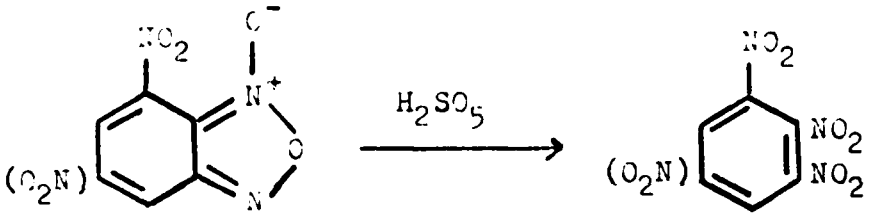
Summary: Monopersulfuric acid oxidized 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene (80 percent) and 4,6-dinitrobenzofuroxan into 1,2,3,5-tetranitrobenzene (quantitative).

Oxidation of 4-nitro- 1[1] and 4,6-dinitrobenzofuroxan 3[1] into 1,2,3-trinitro- 2, mp 120-122°C,[2] (80%) and 1,2,3,5-tetranitrobenzene 4, mp 129-130°C,[3] (99%) extends the only previous oxidation of a furoxan into a dinitro compound,[4] and in combination with the nitration of benzofuroxan,[1] provides a preparative route to vicinal trisubstitution.

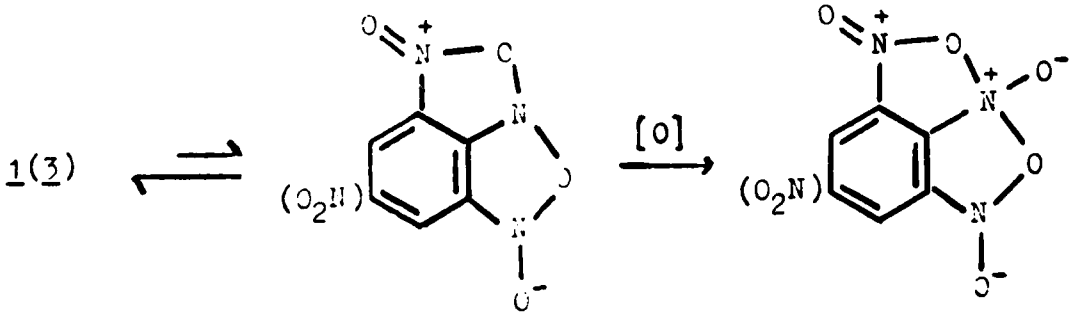
The highly efficient oxidations,[5] 1 → 2[6] and 3 → 4,[7] were brought about by a large excess (over 50 molar) of hydrogen peroxide (90%) in sulfuric acid (98%) at 25°C. for two days. When polyphosphoric acid replaced sulfuric acid the yield of the tetra-

nitrobenzene 4 was moderate (44%) but increased as mixtures of the two acids became enriched in sulfuric acid and became quantitative when only sulfuric acid (80%) was present.

Trifluoroperoxyacetic acid by itself or mixed with concentrated nitric acid failed to react with 4,6-dinitrobenzofuroxan but a mixture of trifluoroacetic and nitric acids and hydrogen peroxide in polyphosphoric acid transformed the furoxan 3 into the tetranitrobenzene 4 in trace amounts.



1(3) 2(4)



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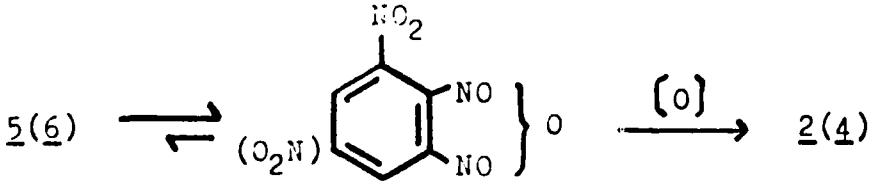

7(8)

Benzofuroxan was oxidized into o-dinitrobenzene (20%) by both trifluoroperacetic[4] and monopersulfuric acid (there was extensive degradation); however, furoxans 1 and 3 resisted oxidation by trifluoroperoxyacetic acid and were recovered. Diminished attraction between the furoxan ring and electrophilic peroxide is the expected result of electron withdrawal into the nitro substituent(s); however, this could be partially balanced by a neighboring group participation by the 4-nitro substituent (see scheme), an effect previously assigned to the degenerate rearrangement of 4-nitrobenzofuroxan and to similar rearrangements.[8] It was assumed that the oxygen atoms were introduced in separate steps. An isomerization with or after the first stage of oxidation of the furoxan 1 or 3 into a nitroso compound, $C_6H_3N_3O_5$ 7 or $C_6H_2N_4O_7$ 8 was not detected; however, a facile oxidation of a nitrosoarene into a nitroarene can be assumed.

Acknowledgement: Financial support was received from the Office of Naval Research.

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3. A.T. Nielsen, R.L. Atkins and W.P. Norris, J. Org. Chem., 1979, 44, 1181 oxidized picramide by hydrogen peroxide (98%) in sulfuric acid (100%) into the tetranitrobenzene 4, mp 127-129°C.

4. J.H. Boyer and S.E. Ellzey, J. Org. Chem., 1959, 24, 2038. The reported procedures were adapted to the present work.

5. The operator must be aware of the danger in handling hydrogen peroxide (90%). Each of these reactions was repeatedly carried out on a scale (1-2 mmol) which called for less than 3 ml (140 mmole) of hydrogen peroxide (90%) without mishap.

6. For the trinitrobenzene 2, nmr(ethyl acetate): δ 8.60-8.75(d,2H) and 8.05-8.30(t,1H); m/e(70 ev): 213 (M^+). For the tetranitrobenzene 4, nmr($CDCl_3$): δ 9.3(s); m/e(70 ev): 258(M^+).

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Part V

Oxidation of Benzodifuroxan into 1,2,3,4-Tetranitrobenzene and 4,7-Dinitrobenzofurazan.

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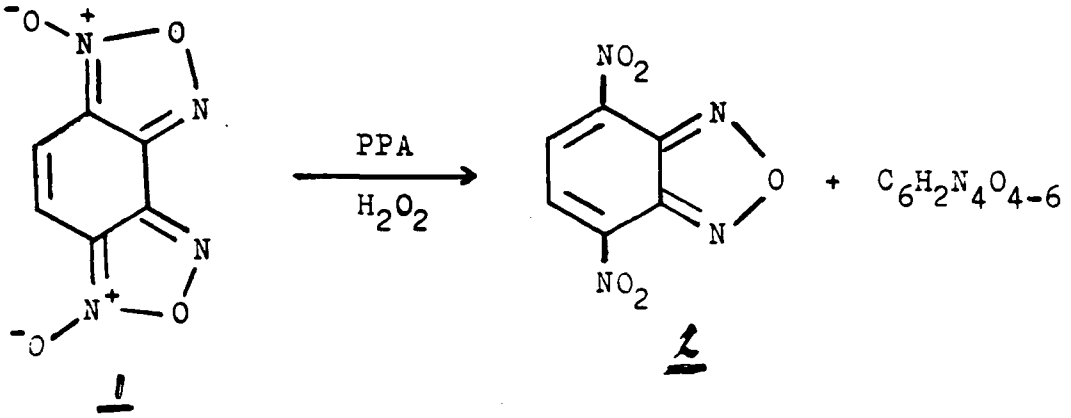
Summary. Benzodifuroxan was oxidized into 4,7-dinitrobenzofurazan and 1,2,3,4-tetranitrobenzene by hydrogen peroxide(90 %) in polyphosphoric acid followed by hydrogen peroxide(90 %) in sulfuric acid(98 %).

A two stage oxidation of benzodifuroxan 1 gave 1,2,3,4-tetranitrobenzene 3, the last of the twelve nitro derivatives of benzene to be prepared.[1] In the milder first stage the difuroxan was oxidized by hydrogen peroxide in polyphosphoric acid into a mixture from which 4,7-dinitrobenzofurazan 2 was partially isolated. The remainder, except for the furazan 2 still present, was oxidized by hydrogen peroxide in sulfuric acid into the tetranitrobenzene 3.[2] Although a complete conversion of the difuroxan 1 could be rapid with extensive degradation (brown gas indicated nitrogen oxides)

when treated with hydrogen peroxide in either sulfuric or trifluoroacetic acid, the mixture obtained in the first stage (assumed to be nitrobenzofuroxans) was less sensitive to degradation and gave the second stage product mixture in which only the tetranitrobenzene 3 and the furazan 2 were detected.



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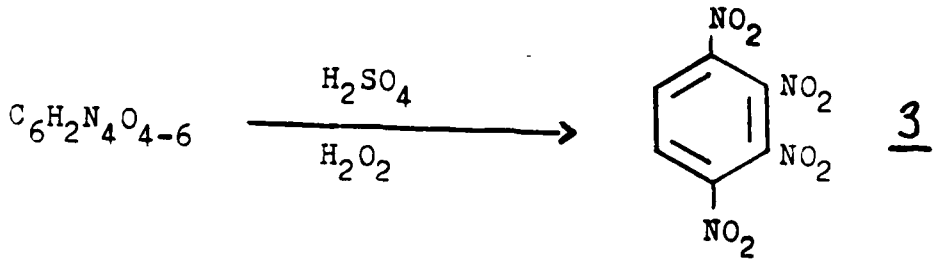

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Hydrogen peroxide (90 %, 4 ml)[3] was added over a period of four hours to a solution of benzodifuroxan[4] (0.22 g, 1.13 mmol) in polyphosphoric acid (10 ml). After stirring at room temperature for two days,[5] ice water was added, and the products extracted into methyl-

ene chloride which was dried (magnesium sulfate), filtered and evaporated to dryness to give a mixture of yellow solids, 0.09 g. Recrystallization from ethyl acetate gave 4,7-dinitrobenzofurazan 2, 0.03 g, mp 187-189°C. [6]

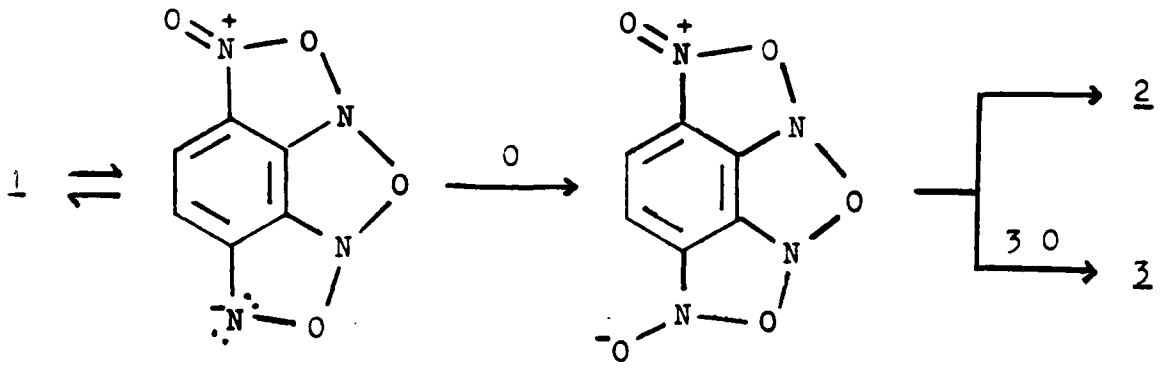
The mixture of yellow solids, 0.09 g in sulfuric acid(98 %, 20 ml) was treated with hydrogen peroxide (90 %, 2 ml) added slowly over a period of two hours. The reaction mixture was stirred at room temperature for three days and worked up in the manner described above. Removal of methylene chloride left a yellow solid. 1,2,3,4-Tetranitrobenzene 3 was extracted by, and then recrystallized from, carbon tetrachloride as a yellow solid, 0.03 g(12 %)mp 108-109°C.[6]

The portion insoluble in carbon tetrachloride gave the furazan 2, 0.05 g, mp 187-189°C after recrystallization from ethyl acetate (combined yield 21 %).

The identification of 4,7-dinitrobenzofuroxan 2 was consistent with a single nmr ^1H signal (ethyl acetate) at δ 8.52 for the two equivalent hydrogen atoms at positions 5 and 6, by ir absorption (potassium bromide) for the nitro groups at 1530 and 1340 cm^{-1}; by verification of the molecular weight, elemental analysis and resistance toward oxidation by Caro's

acid. The structure of 1,2,3,4-tetranitrobenzene 3 was supported by a single nmr ^1H signal (ethyl acetate at δ 8.65, by ir absorption (potassium bromide) at 1565 and 1340 cm^{-1} (nitro group), verification of the molecular weight and elemental analysis.

Neighboring group participation between furoxan noieties can account for a terminal monooxidation by a cleavage of two oxygen bridges in the intermediate 4 and for further oxidation by bonding an oxygen atom to tervalent nitrogen in 4. The penultimate oxidation level, $C_6H_2N_4O_7$, was assumed to be a mixture of two nitrosotrinitrobenzene isomers which readily oxidized into the product 3.



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Acknowledgment: Financial support was received from O. N. R. The n.m.r. spectra were obtained from a Bruker 270MH instrument at the University of Chicago, Chicago, Illinois.

Footnotes and references.

1. Joseph H. Boyer and Chorngbao Huang, J. Chem. Soc. Chem. Commun. reported peracid oxidations of benzofuroxan, 4-nitro- and 4,6-dinitrobenzofuroxans.

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3. Hydrogen peroxide(90 %) must be handled as a dangerous reagent. The compounds $C_6H_2N_4O_{4-8}$ are potentially explosive.

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5. The disappearance of starting material was monitored by ir.

6. Satisfactory elemental analyses for C, H and N (Micro Tech Laboratories, Inc., Skokie, Ill.), molecular weights by mass spectrometry (AEI Scientific Limited MS 30, 70 eV, source temperature 120-150°C) and n.m.r. data (Bruker 270M instrument) were obtained for the new compounds 2 and 3.

Part VI

THE AMBIPHILIC FUROXAN RING. BENZOFUROXAN OXIDATION BY PERACID AND REDUCTION BY COPPER.[1]

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Abstract.

Monopersulfuric acid, trifluoroperacetic acid and hydrogen peroxide in polyphosphoric acid, or with selenium dioxide in t-butyl alcohol, or in tetramethylene sulfone have each oxidized benzofuroxan into o-dinitrobenzene. Monopersulfuric acid oxidized 4-nitrobenzofuroxan into 1,2,3,5-tetranitrobenzene(99 %); hydrogen peroxide in polyphosphoric acid was moderately efficient for the latter oxidation. Copper in acidified ethanol transformed 4,6-dinitrobenzofuroxan into picramide quantitatively.

Introduction.

A. General. Although 1a ⇄ 1b abbreviated to 1a or 1b is the accepted symbol for benzofuroxan,[2,3]

it tends to disguise the disposition toward electron donation and acceptance shown by the heterocyclic ring.

Dinitrogen tetroxide, manganese dioxide in acetic acid, and nitric acid have oxidized oximes into nitronic acids 2 or the tautomeric nitro compounds,[4,5] but failed to oxidize the heterocyclic ring in the furoxan 1, an oxime-nitronic acid anhydride. Peracetic and perbenzoic acids have fragmented trialkylhydroxylamines, presumably via initial oxidation into a hydroxylamine-N-oxide 3,[6] but failed to oxidize the heterocyclic ring in the furoxan 1, a latent hydroxylamine by virtue of 1c ↔ 1d ↔ 1a ↔ 1b.

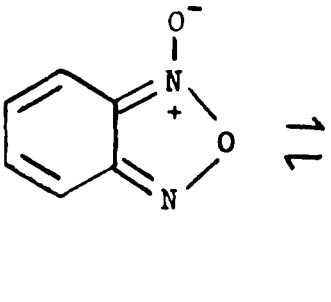
Resistance toward N-oxidation is also characteristic of isoxazoles 4, isoxazolines 5, furazans 6, and presumably other oxime esters, both cyclic and linear;[7] however, the contrary is implied by the extended principle of the α-effect.[8]

B. Electron Donation. On the other hand, trifluoroperoxyacetic acid was successful, where performic and peracetic acids were not,[9] in oxidizing benzofuroxan into o-dinitrobenzene 7 and 5-methylbenzofuroxan into 3,4,-dinitrotoluene; but the efficiencies (15-20 %) were in marked contrast with the similar oxidation of p-di-

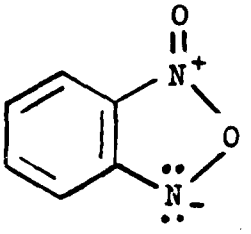
nitrosobenzene into p-dinitrobenzene (92 %).[10] Extensive degradation of naphtho- and phenanthrofuroxan and 5-chloro-6-methoxybenzofuroxan, attributable to oxidation initiated at carbon atoms, occurred without affording detectable amounts of nitro compounds.[10]

An older,[11] discredited,[12] claim for oxidation of oximes by monopersulfuric acid (Caro's acid) has now been indirectly supported by an oxidation of benzofuroxan by hydrogen peroxide in sulfuric acid.

Unsymmetrical diarylfuroxans 8 were fragmented and oxidized into aromatic acids when treated with ozone. A preferential electrophilic attack by ozone on the N-oxide side of the heterocycle was invoked.[13,14]



1a ⇌ 1b



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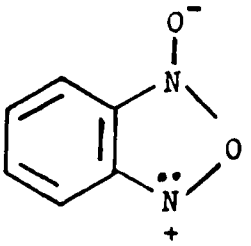

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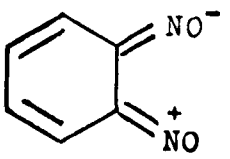

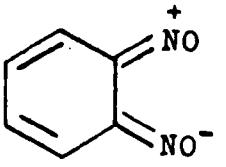

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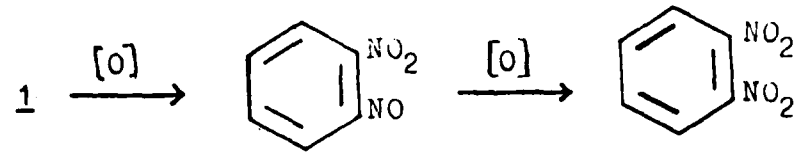

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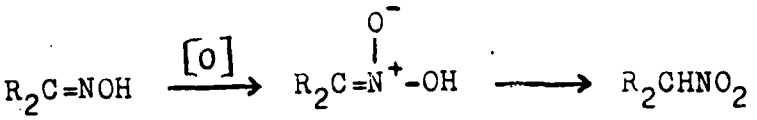

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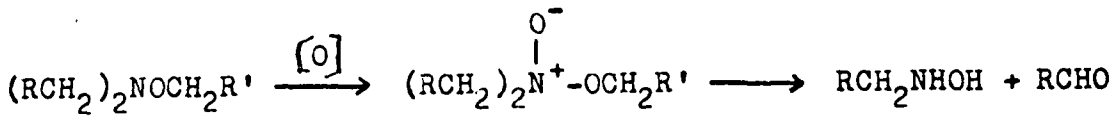

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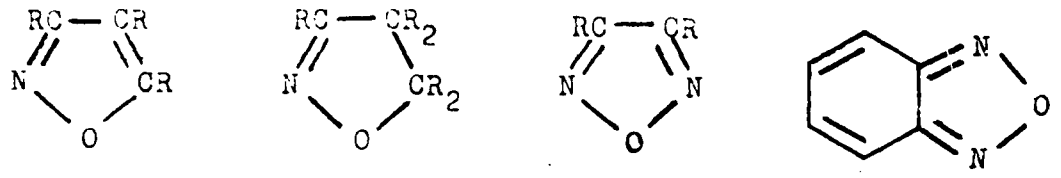

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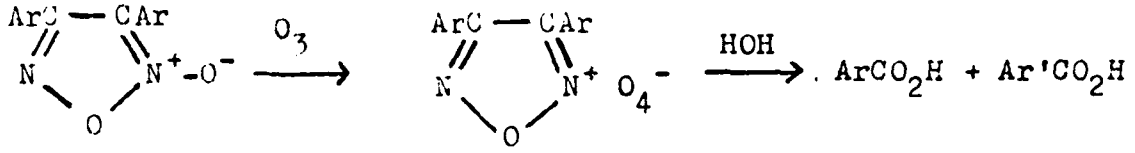
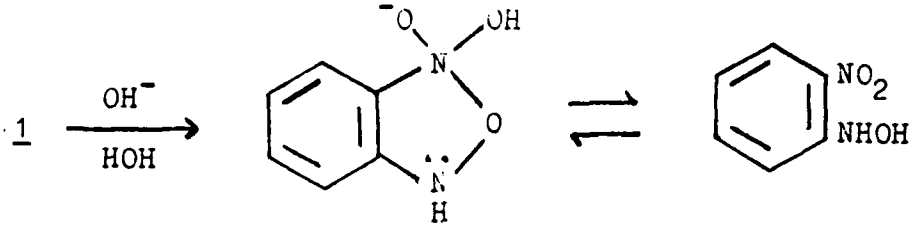


8

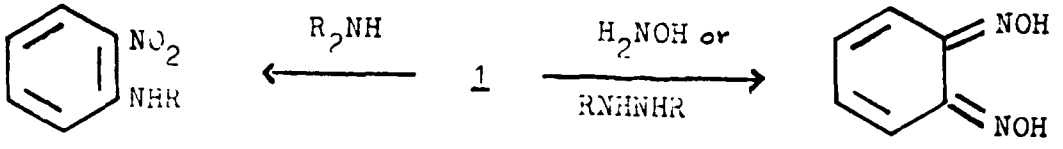
C. Electron Acceptance. An addition of water to benzofuroxan (an anhydride) [redacted] is unknown; however, the adduct 9 ⇄ 10 is related to a nitrosonium hydroxide 11a ⇄ 11b, recently reported.[15] Electron acceptance at a furoxan nitrogen atom, related to the re-

quirement for the formation of the adduct 9 has been demonstrated in the transformation of a benzofuroxan into an o-nitrophenylhydrazine by a secondary amine,[16] and in the reduction of a benzofuroxan into a dioxine by either hydroxylamine,[17] a hydrazine[18] or copper.[2b]



9 10

11a 11b



Results and Discussion. o-Dinitrobenzene 7 was obtained from benzofuroxan 1 and hydrogen peroxide (90 %) in polyphosphoric or sulfuric(80 %) acids or in tetramethylene sulfone, and with hydrogen peroxide (90 %) and selenium dioxide in t-butyl alcohol. Although protonation of benzofuroxan, pKa -8.3,[19] in sulfuric acid (98 %, pKa -10.3; 80 %, pKa -7.5)[20] can

be assumed, its assistance, if any, to the oxidation was not determined. Just as the location of protonation has not been established,[21] it is not possible to differentiate between peroxide attack at a nitrogen or an oxygen atom in the oxidation of a benzofuroxan into an o-dinitrobenzene. It was assumed that the formation of new carbon-oxygen bonds by either electrophilic or nucleophilic attack initiated extensive degradation.

In a mixture of nitric acid and hydrogen peroxide benzofuroxan afforded 4-nitro- 12 and 4,6-dinitrobenzofuroxan 14 but neither o-dinitrobenzene 7 nor nitrated derivatives, e.g., 13 and 15, were detected. Apparently an electrophilic attack on the heterocyclic portion of the molecule by a peroxide or other oxidant was not competitive with nitration and the peroxides present did not attack the furoxan ring in the nitro compounds 12 and 14. Degradation was attributed to oxidation at carbon atoms in compounds 1, 12 and/or 14.

Benzofurazan 16 and diphenylfuroxan 8 (Ar = Ar' = C_6H_5) were each unreactive toward monopersulfuric acid (the most effective peroxide reagent) and other peroxides.

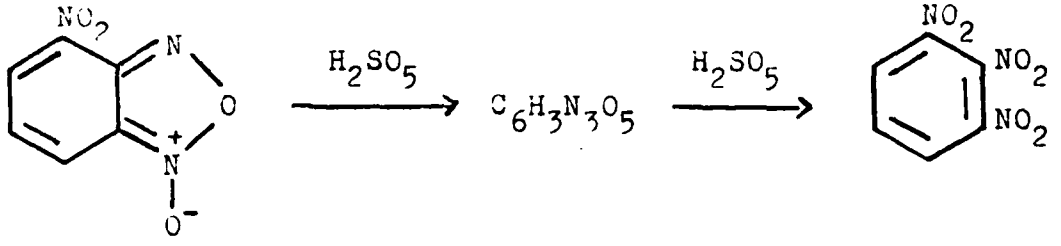
With an absence of extensive peroxidative degradation, 4-nitro- 12 and 4,6-dinitrobenzofuroxan 14

gave 1,2,3-trinitro- 13 and 1,2,3,5-tetranitrobenzene 15 in excellent to quantitative yields when treated with hydrogen peroxide(90 %) in concentrated sulfuric acid(98 %). These are attractive preparative procedures however the danger associated with hydrogen peroxide (90 %) must be recognized. An inability of trifluoro-peroxyacetic acid to oxidize either furoxan, 12 or 14, is partially attributable to a deactivation of the furoxan ring nitrogen and oxygen atoms by the nitro substituent(s). The superior performance of mono-persulfuric acid was revealed by the investigations on 4,6-dinitrobenzofuroxan in mixtures of sulfuric acid and polyphosphoric acids. When only poly-phosphoric acid was present the yield of the tetra-nitrobenzene 15 was 44 %; when only sulfuric acid was present the yield was 100 % (Table I). Oxidative degradation may partially account for the deficiency in mass balance for reactions in polyphosphoric acid. The greater reactivity of the mononitrofuroxan 12 was shown in a series of experiments in which mixtures of 12 and the dinitrofuroxan 14 competed for oxidation. A large molar excess (40 to 80) of peroxide was required for satisfactory efficiency. (Table II).

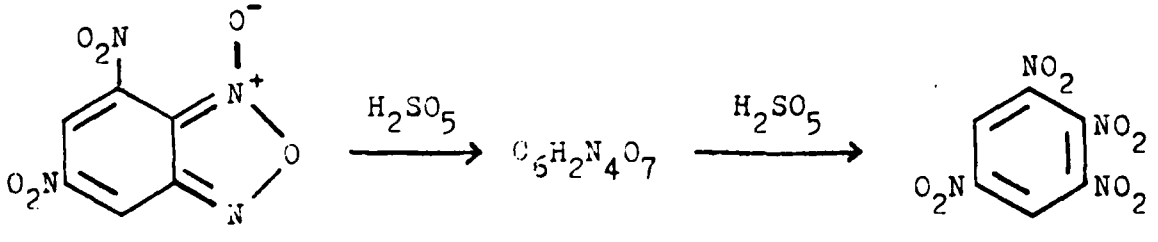
TABLE I.

TABLE II.

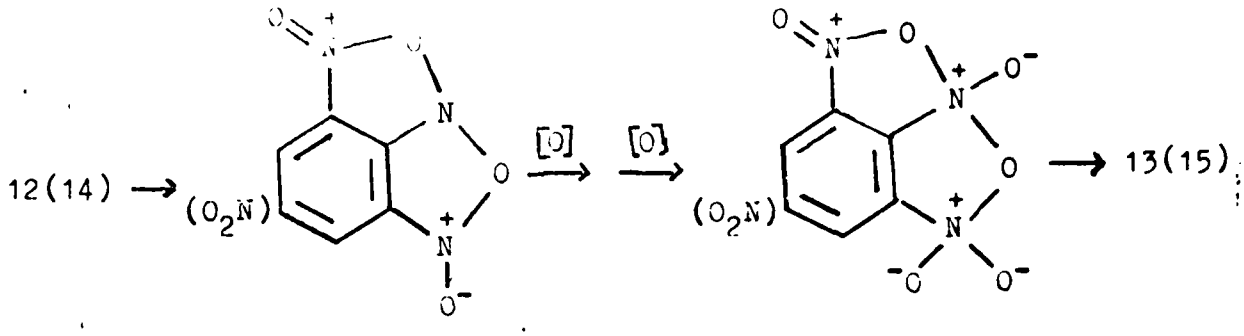
Two stages in the oxidation of benzofuroxan into a polynitro compound via a nitrosonitro intermediate, e.g., 17, were probably involved. A retardation at either stage may reflect deactivation by electron withdrawal into (the) nitro substituent(s) in compounds 12 and 14.[22] On the other hand there may be a balancing activation by a neighboring group participation of the 4-nitro substitutent, cf. 18 and 19.[23] Further insight will be sought by investigating the oxidation of 5-nitrobenzofuroxan into 1,2,4-trinitrobenzene.



12 13

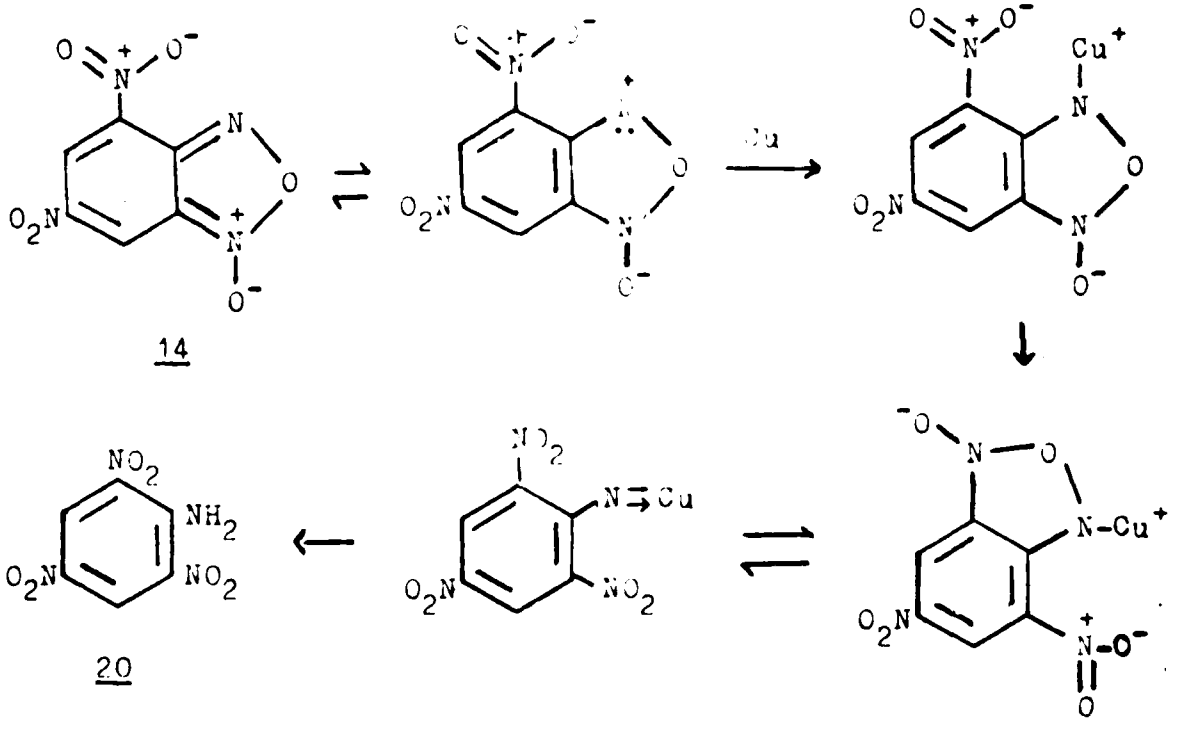


14 15



18 19

A highly specific quantitative reduction of 4,6-dinitrobenzofuroxan 14 into picramide 20 without the formation of a detectable amount of an isomeric amine by treatment with copper bronze in ethanol is now reported.[2b] In a transfer of an electron from copper to the heterocyclic ring, a control in the selection of the nitrogen atom to be bound to copper is provided by electronic and steric factors associated with the 4-nitro substituent as shown in the scheme.



14 20

Experimental Section. The infrared spectra were recorded on a Perkin Elmer grating infrared spectrophotometer model 237B or 521. NMR spectra were obtained on a Varian A-60 or T-60 spectrometer with TMS as an internal standard. Mass spectra were recorded on AEI Scientific Apparatus Limited MS 30 double beam mass spectrometer at 70 ev with source temperature 120-150°C. Elemental analyses were carried out by Micro Tech Laboratories, Inc., Skokie, Illinois.

The following compounds are commercially available: benzofuroxan, mp 69-71°C, hydrogen peroxide, 90 %, d = 1.54; o-dinitrobenzene, mp 117-118°C; selenium dioxide, mp 315°C; tetramethylene sulfone, mp 27°C; 4-chloro-2-nitroaniline, mp 115-116°C; m-dichlorobenzene, bp 172-173°C; benzil, mp 94-95°C.

The following compounds were prepared according to the literature: 4,6-dinitrobenzofuroxan, mp 171-172°C;[24] 4-nitrobenzofuroxan, mp 142-143°C;[24] polyphosphoric acid;[25] benzofurazan, mp 55-56°C;[26] diphenylfuroxan, mp 117-118°C.[27]

Except where otherwise specified a product yield was based on recovered starting material.

Oxidation of benzofuroxan in polyphosphoric acid. To a solution of benzofuroxan (1.36 g, 10 mmol) in

polyphosphoric acid (30 ml), hydrogen peroxide(90 %, 3 ml, 123 mmol) was added dropwise at 0°C over a period of 4 h, and stirred for 18 h at room temperature, and 24 h at 60-65°C. The reaction mixture was diluted with ice water and extracted with methylene chloride. The extracts were dried with magnesium sulfate, filtered, and concentrated to dryness to give o-dinitrobenzene mp 115-117°C[10] (0.41 g, 2.5 mmol, 25 %).

A similar treatment in sulfuric acid(80 %, 20 ml) and hydrogen peroxide(90 %, 1 ml, 41 mmol) afforded 0.22 g(13 %) of o-dinitrobenzene, mp 117-118°, from benzofuroxan (1.36 g, 10 mmol).

Nitration of benzofuroxan in nitric acid(70 %), free of nitrous acid, and hydrogen peroxide(90 %) at 0°C for 6 h and stirring for 3 days at 25°C afforded 4-nitrobenzofuroxan, mp 142-143°C (40 %) and 4,6-dinitrobenzofuroxan, mp 171-172°C (21 %). An unidentified pale yellow solid, mp 126-130°C, soluble in water and in methanol(60 %) was also obtained.

Benzofuroxan gave o-dinitrobenzene(17 %) when oxidized by hydrogen peroxide(90 %) in tetramethylene sulfone or by hydrogen peroxide(90 %) and selenium dioxide in t-butyl alcohol. In 16 and 56 % amounts, benzo-

furoxan was respectively recovered.

Oxidation of 4,6-dinitrobenzofuroxan in sulfuric acid. To a solution of 4,6-dinitrobenzofuroxan (0.50 g, 2.2 mmol) in sulfuric acid(98 %, 30 ml), hydrogen peroxide(90 %, 4 ml, 164 mmol) was added dropwise at 0°C over a period of 4 h and stirred for 3 days at room temperature. Methylene chloride extractions from the reaction mixture diluted with ice water were dried ($MgSO_4$), filtered and concentrated to dryness to give a yellow solid mixture, 0.56 g. Nmr analysis showed the presence of 1,2,3,5-tetranitrobenzene, 0.51 g (99 %) and 0.05 g (10%) of 4,6-dinitrobenzofuroxan. Recrystallization from chlorofo gave 1,2,3,5-tetranitrobenzofuroxan, mp 126-127°C,[28] nmr($CDCl_3$): δ 9.3(s), m/e 70ev: 258(M^+).

A similar treatment transformed 4-nitrobenzofuroxan into 1,2,3-trinitrobenzene, mp 120-122°C[29] (80 %) after recrystallization of the residue obtained by evaporating to dryness a methylene chloride solution; nmr(ethyl acetate): δ 8.60-8.75(d,2 H) and 8.05-8.30 (t,1 H); m/e (70 ev): 213(M^+).

Oxidation of 4,6-dinitrobenzofuroxan in mixtures of sulfuric and polyphosphoric acids. To a solution of 4,6-dinitrobenzofuroxan (0.50 g. 2.2 mmol) in a mixture

of sulfuric(98 %) and polyphosphoric acids (30 ml), hydrogen peroxide (90 %, 3 ml, 123 mmol) was added dropwise at 0°C over a period of 4 h, and stirred for 3 days at room temperature. Methylene chloride extractions, obtained from the reaction mixture diluted with ice water, were dried with magnesium sulfate, filtered, and concentrated to dryness to give a yellow solid mixture. Analysis by nmr quantitatively established the presence of 1,2,3,5-tetranitrobenzene and starting material. The results are presented in Table I.

Reduction of 4,6-dinitrobenzofuroxan 14 by copper.[30]

To the furoxan (1.0 g, 4.4. mmol) in methanol (100 ml) copper (0.422 g, 67 mmol), or copper bronze powder, and hydrochloric acid(37 %, 1 ml) were added. The mixture was heated to reflux for 22 h and filtered. The filtrate was combined with an acetone wash of the precipitate and concentrated by evaporation and the residue isolated by chromatography from an alumina column or by recrystallization to give picramide, mp 188-190°C,[31] 0.88 g(87 %). When the reaction was run in ethanol the yield was 80 %.

Acknowledgment: Partial financial support was received from the Office of Naval Research.

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30. This experiment was carried out by Mr. Tien-Teh Chen.

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TABLE I

Oxidation of 4,6-Dinitrobenzofuroxan 14 in mixtures of sulfuric and polyphosphoric acids (PPA) and hydrogen peroxide.[a]

Run number	Volume, %		Product mixture, g	Recovered 13, %[d]	Product 17 yield, %[d]
	H_2SO_4[b]	PPA[c]			
1	0	100	0.45	83	44
2	10	90	0.48	90	50
3	30	70	0.47	90	55
4	50	50	0.47	87	50
5	80	20	0.47	52	76
6	90	10	0.53	40	97
7	100	0	0.54	33	100

[a] In each run there was 0.5 g (2.8 mmol) of the furoxan 14 and 3.0 ml (123 mmol) of H_2O_2 (90 %) in 30 ml of acid or acid mixture. [b] 98 %. [c] ref. 25. [d] The composition of each product mixture in ethyl acetate was determined by an nmr analysis with authentic samples as standards. The yield of nitro compound 15 was based on converted starting material.

TABLE II

Oxidation of Equimolar[a] Mixtures of 4-Nitrobenzofuroxan 12 and 4,6-Dinitrobenzofuroxan 14 in Monopersulfuric Acid[b]

Run number	Hydrogen Peroxide, ml	Time, days	Recovered furoxans (%)[c]	Nitro compounds (%)[c]
1	2[d]	1	12 (0)	13 (80)[e]
			14 (73)	15 (27)[f]
2	2[d]	2	12 (0)	13 (78)[e]
			14 (70)	15 (30)[f]
3	1[g]	1	12 (trace)	13 (75)[e]
			14 (80)	15 (20)[f]
4	1[g]	2	12 (trace)	13 (78)[e]
			14 (72)	15 (28)[f]

[a] 2.2 mmol of 12 and of 14. [b] 30 ml H_2SO_4 (98 %). [c] Each mixture of furoxans and nitro compounds was quantitatively analyzed by nmr (ethyl acetate) with authentic compounds as standards. Yields are based on 2.2 mmol of starting material. [d] 82 mmol. [e] Degradation of 12 assumed. [f] Quantitative yield based on recovered starting material. [g] 41 mmol.

VII. Other Results

Table I summarizes investigations on the oxidation of diaminomaleonitrile and its derivatives.

The oxime 1 of ketonitro succinonitrile was obtained as the pyridinium salt 2 of an oxime O-benzoyl ester in four steps[1] from nitromethane. An investigation of its oxidation into a dinitrosuccinonitrile 3 and dinitromaleo(fumaro)nitrile 4 is underway.

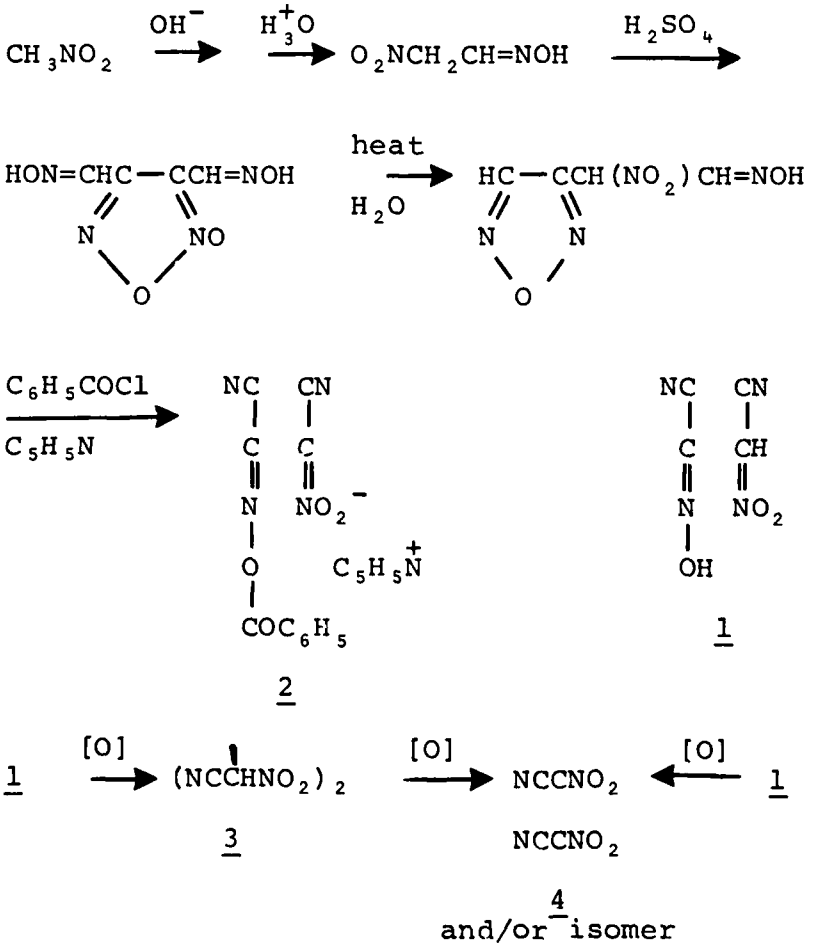


Table I

DAMN[a] Derivatives, $H_2NC(CN)=C(CN)NRR'$, and Oxidants

R R'	Oxidant Solvent	Hours[b] t, °C	Product, % yield
H H	H_2O_2[c] CH_3COCH_3	2 60	$(CONH_2)_2$,[d,e] 78
H H	H_2O_2[c] CH_2Cl_2	0.2 25	$(CONH_2)_2$,[d,e] 43
H H	H_2O_2[c] THF	16 25	_____[f]
H H	H_2O_2[c] $CHCl_3$	0.1 25	$(CONH_2)_2$,[d,e] 80
CH_3CO H	H_2O_2[c] CH_3OH	40 25	$(CONH_2)_2$,[d,e] 31
$=CHC_6H_4OCH_3$-p	CF_3CO_3H CH_2Cl_2	1 39	Trace, unidentified.
$=CHC_6H_4OCH_3$-p	MCPBA $CHCl_3$	16[g] 61	Recovered 35% s.m. Intractable mixture.
$=CHC_6H_4OCH_3$-p	H_2O_2[c,h] CH_3OH, CH_3CN	20 45	Recovered 5% s.m. Intractable mixture.

Table I cont'd.

$=CHC_6H_4OCH_3$-p	H_2O_2[c]	16	Recovered s.m.
	THF,CH_3CN	56	quantitatively.
$=CHC_6H_4OCH_3$-p	H_2O_2[c]	0.1	Intractable
	CH_3CO_2H[i]	118	mixture.
H	DABCO·$2H_2O_2$	7	Unidentified,[j]
H	THF	56	mp 134-136°.
H	RCO_3H[k]	1	$NCCONH_2$, 10%.
H	CH_2Cl_2	39	mp 60-62°.[l]
CH_3CO	DABCO·2H O	16	$C_6H_8N_4O_2$, 35%,
H	THF	25	mp 260°
$=CHC_6H_5$	DABCO·$2H_2O_2$	10[3]	$C_{11}H_{10}N_4O$, 66%,
	THF	25	mp 225-7°(dec).
C_6H_5	CF_3CO_3H	1	Trace,
C_6H_5	CH_2Cl_2	39	unidentified.
$=CHC_6H_4OCH_3$-p	MCPBA	16[g]	Rec. s.m. 16%
	CH_2Cl_2	80	Intractable mix.
$=CHC_6H_4OCH_3$-p	H_2SeO_3	0.25	_____m
	CH_3CO_2H	118	
H	H_2SeO_3	0.25	_____n
H	CH_3CO_2H	40	
$=CHC_6H_4OCH_3$-p	H_2O_2[c]	64	_____p
	CH_3OH[o]	25	
$=CHC_6H_4OCH_3$-p	DABCO·$2H_2O_2$	16	Rec. s.m. 100%
	THF	25	

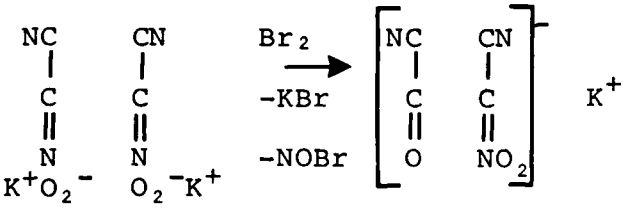
Table I cont'd. Legend.

[a]Diaminomaleonitrile. [b]Time required for disappearance (monitored by tlc) of DAMN or a derivative. [c]Commercial reagent, 90% in 6-60 molar excess. [d]Thermal decomposition without melting > 350°C; authentic mp 420°C(dec). Titration of derived oxalic acid against permanganate confirmed identification. Ir absorption 3360 (broad, s, NH), 3160 (broad, s), 1650 (broad, s, CO), 1340(s) and 1095 cm^{-1} (m). MS: 88(100) M^+, 70(60) and 60(50). [e]No other product detected by tlc. [f]Starting material detected by tlc. [g]Optimum conditions not established. [h]With an equimolar amount of sodium tungstate. [i]Other solvent systems also investigated: CH_3CO_2H and HNO_3, CF_3CO_2H, CF_3CO_2H and HNO . [j]By tlc and ir this product resembles DAMN. [k]Monopermaleic acid. [l]Also a trace amount of known 2-amino-3,5,6-tricyanopyrazine, mp 220-222°C(dec). (R. G. Begland D. R. Hartter, D. S. Donald, A. Cairncross and W. A. Shephard, J. Org. Chem., 1974, 39, 1235). [m]Two products: 3,4-dicyano-1,2,5-selenadiazole, 66%, mp 96-97°C (D. Shew, Thesis, Indiana Un., 1959; Disser. Abstr., 1959, 20, 1593) and 4,5-dicyano-2-p-anisylimidazole, 7%, mp 231-233°C; ir(KBr): 3180(br), 2260, 2235, 2220 and 1610 cm^{-1}; nmr ($(CD_3)_2CO$): δ 3.9 (s, 3H), 7.1 and 8.0 (AB quartet, 4H), 7.5-7.7 (br, 1H, exchanged by D_2O); m/e(70 ev): 224(100M^+,

Table I cont'd. Legend.

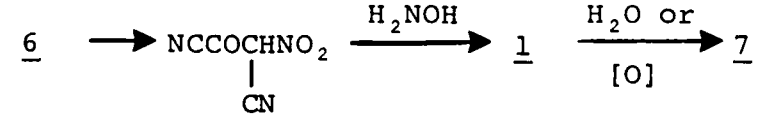
209(21), 181(30). This new compound was obtained in insufficient amount for elemental analysis. The structure assignment is tentative. [n]3,4-Dicyano-1,2,5-selenadiazole, mp 96-97°C, 82% (see m). [o]With a catalytic amount of NaOH. [p]$C_{12}H_{12}N_4O_1$, mp 213-216°C, in agreement with $\underset{\uparrow}{p}CH_3OC_6H_4CH{=}NC(CN){=}C(NH_2)CONH_2$ reported by Y. Ohtsuka, J. Org. Chem., 1979, 44, 827.

A product 6 from the recently reported dipotassium salt 5 of vic-dinitrosuccinonitrile and bromine appears to be the potassium salt of ketonitrosuccinonitrile,[3,4] this tentative assignment is based on elemental analysis (C,N,O) and ir spectrum (KBr): 2220w (C≡N), 1645m (C=O), 1585s and 1330s cm^{-1} (NO_2). Direct analysis for potassium and for a mass spectrum will soon be obtained.



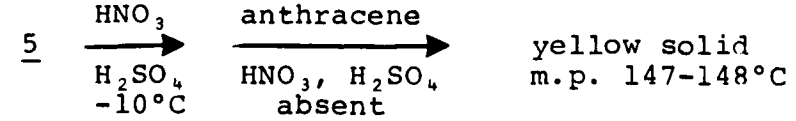
5 6

Transformations of 1 and ketonitrosuccinonitrile 7 into each other are underway:

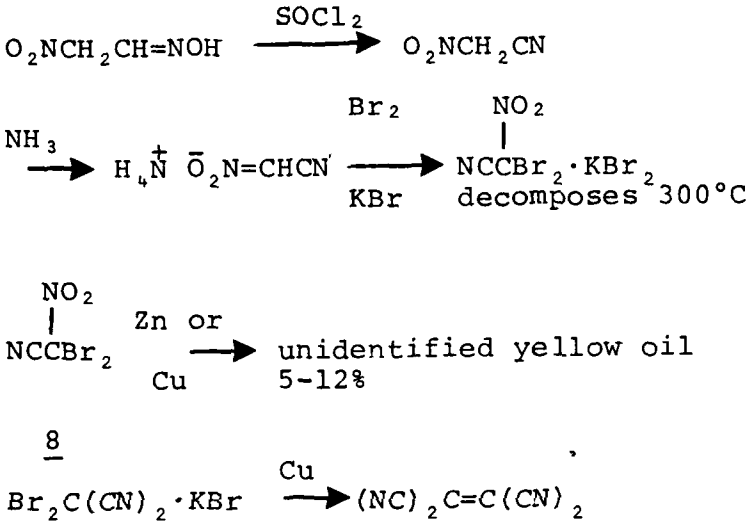


7

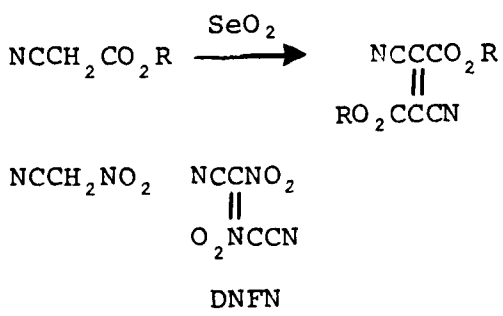
Nitric acid has efficiently transformed the dipotassium salt 5 into a product. Its identification is underway.[5]



Reductive dimerization of dibromonitroacetonitrile 8 into compound 4 by treatment with zinc or copper powder was unsuccessful. In contrast tetracyanoethylene was obtained in high yield from dibromomalononitrile in a similar reaction.[6]

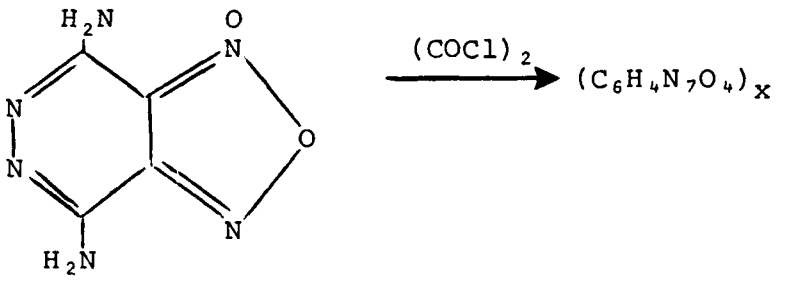


Although an oxidative dimerization of ethyl cyanoacetate produced diethyl dicyanofumarate[7] as shown ($R=C_2H_5$), similar oxidative dimerization of nitroacetonitrile into dinitrofumaronitrile, DNFN, was not detected although a wide range of experimental conditions was employed. Starting material was recovered almost quantitatively.



Intractable mixtures were obtained from the potassium bromide -dibromonitroacetonitrile complex when treated with hexamethyl phosphorus triamide in methylene chloride,[8] potassium thiocyanate in dimethylformamide[9] or copper in the presence of an olefin, e.g., cyclohexene or a diene, e.g., cyclopentadiene.[10] Triphenylphosphine abstracted oxygen from the complex to form triphenylphosphine oxide apparently without the occurrence of a competitive debromination; a mixture of triphenylphosphine and silver nitrate[11] also produced triphenylphosphine oxide and silver bromide was formed.

Preliminary results of two reactions of 4,7-diamino-5,6-diazabenzofuroxan 9 are reported. Oxalyl chloride produced a colorless solid, $(C_6H_4N_7O_4)_x$, mp 350°. Further investigation is planned.



Iodobenzenediacetate ($C_6H_5I(OAC)_2$) in benzene and the diamine 7 produced a strong transient green color, an expected characteristic of an intermediate nitroso compound. A detailed investigation of the nearly colorless solid product is planned.

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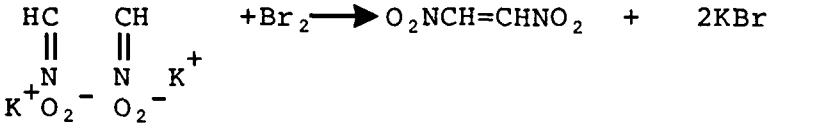

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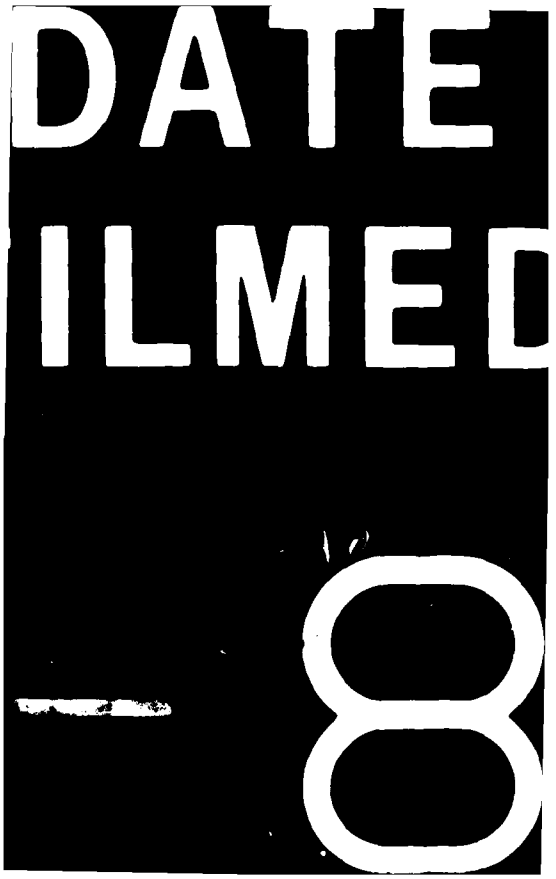
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